

# Studying The Catalytic Properties Of The Synthesized Hydrotreatment Catalyst Carriers Using Palygorskite Clay

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**Abstract:** Prerequisites of the problem. Diesel fuel hydrogenation catalysts are imported from abroad. Creation of technology for production of such catalysts based on local raw materials and production wastes is an urgent problem.

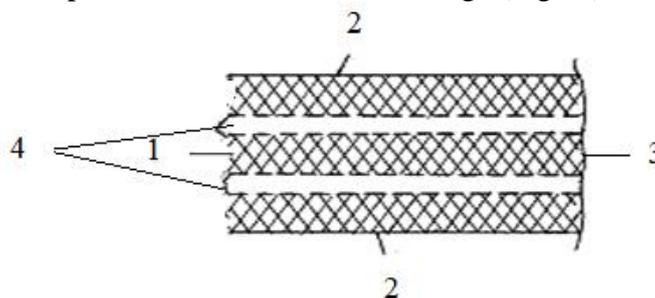
**Keywords:** hydrotreatment, aluminum-nickel-molybdenum catalyst, carbonate palygorskite, hydrogenation, carrier, diesel fuel.

## 1. Introduction

Hydrotreating processes of oil fractions, which include hydrotreating and hydrocracking, are the most large-scale oil refining processes and are key to the production of motor fuels that meet the requirements of modern environmental standards. In accordance with this, the sulphur content in the produced diesel fuel should not exceed 10 mg/kg, the content of polycyclic aromatic compounds - not more than 8 wt%, cetane number - not less than 51 [1].

Aluminum-nickel-molybdenum catalysts use active aluminum oxide as a carrier of active components, which content in the catalyst is 80-82%. In the process of obtaining the active aluminum oxide, large amounts of environmentally hazardous waste water are formed in the form of salt solutions. The construction of special treatment plants is required to purify waste water and utilize other wastes, which results in higher production costs. The replacement of an expensive carrier - active aluminum oxide - with affordable, cheap carriers that are not inferior in physical and chemical properties is an urgent task.

One of the most important properties of natural clays is their ion-exchange and sorption properties. During the dehydration of natural clays by heating meso- and micropores are released, as a result, it absorbs molecules of various substances. In the author's opinion [2], there are three groups of reasons that determine the ion-exchange properties of clay minerals. The first group includes substitutions within the structure of minerals, under the influence of processes in the nature of  $\text{Si}^{4+}$ , can be replaced by  $\text{Al}^{3+}$ . Breaking of bonds around the edges of aluminosilicon units of the mineral structure is singled out into the second group of causes that determine the cation exchange capacity. Bond disruption can occur when the crystal lattice is broken, for example, as a result of mineral change (Fig. 1).



**Fig. 1. Crystallite of clay mineral: 1 Elementary Package; 2-Chipped Surface (surface of 1st generation); 3-Basal Surface (surface of 2nd generation); 4-Surface of individual packages (surface of 3rd generation).**

The third group includes substitution of external hydroxyl hydrogen by exchange cations. When the crystal lattice of minerals is destroyed, some hydroxyl groups are detected. Exchange cations, sorbed as a result of such violations on the side surfaces, at least partly, hydrogen outdoor hydroxyl.

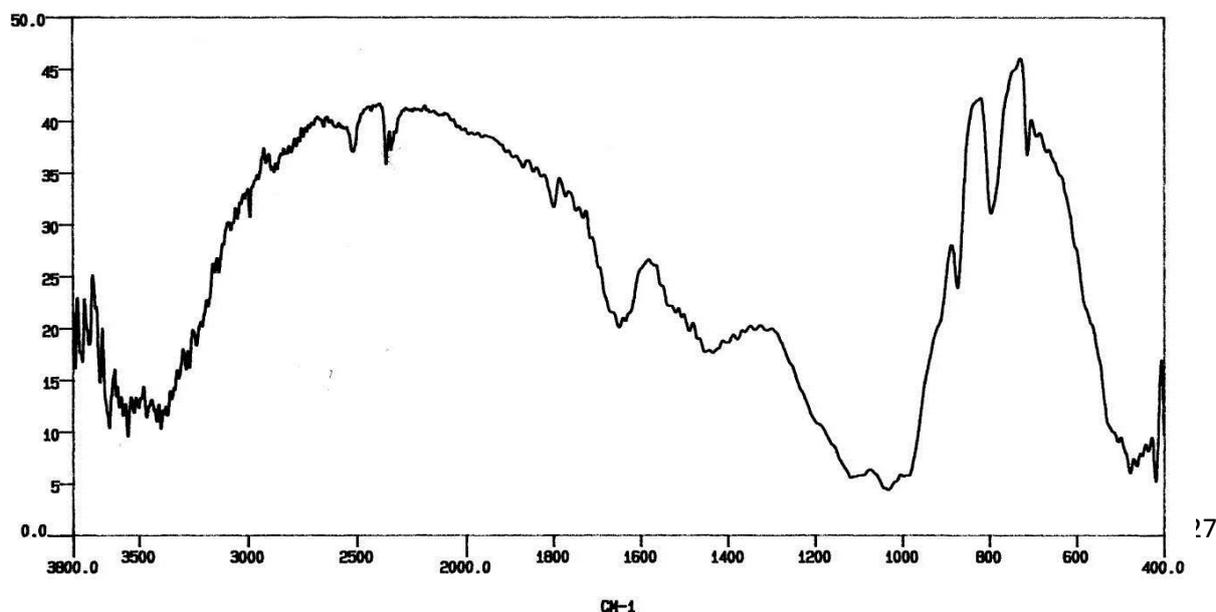
For the purpose of development of technology for synthesis of a new catalyst for hydrotreatment of diesel fuel the following components have been selected as initial components: carbonate-Palygorskite clay, aluminum hydroxide, nickel and molybdenum compounds. Hydrotreating phase - nickel is used in combination with molybdenum as nickel salt of molybdenum acid. The use of  $\text{MoO}_3$  as a second component allows to stabilize the hydrating properties and improve the functionality of the contact, as  $\text{MoO}_3$  simultaneously has hydrodehydrating and acidic properties, in the sulfide form, these functions are further enhanced. It was found that the nickel salt of molybdenum acid has multifunctional properties and is the most active catalyst for hydrogenation, isomerization, dehydrocycle, destructive hydrogenation and waterproofing of petroleum products of different origin [3]. Treatment of the catalyst with sulfur or hydrogen sulfide increases its activity in acid catalysis [4-6].

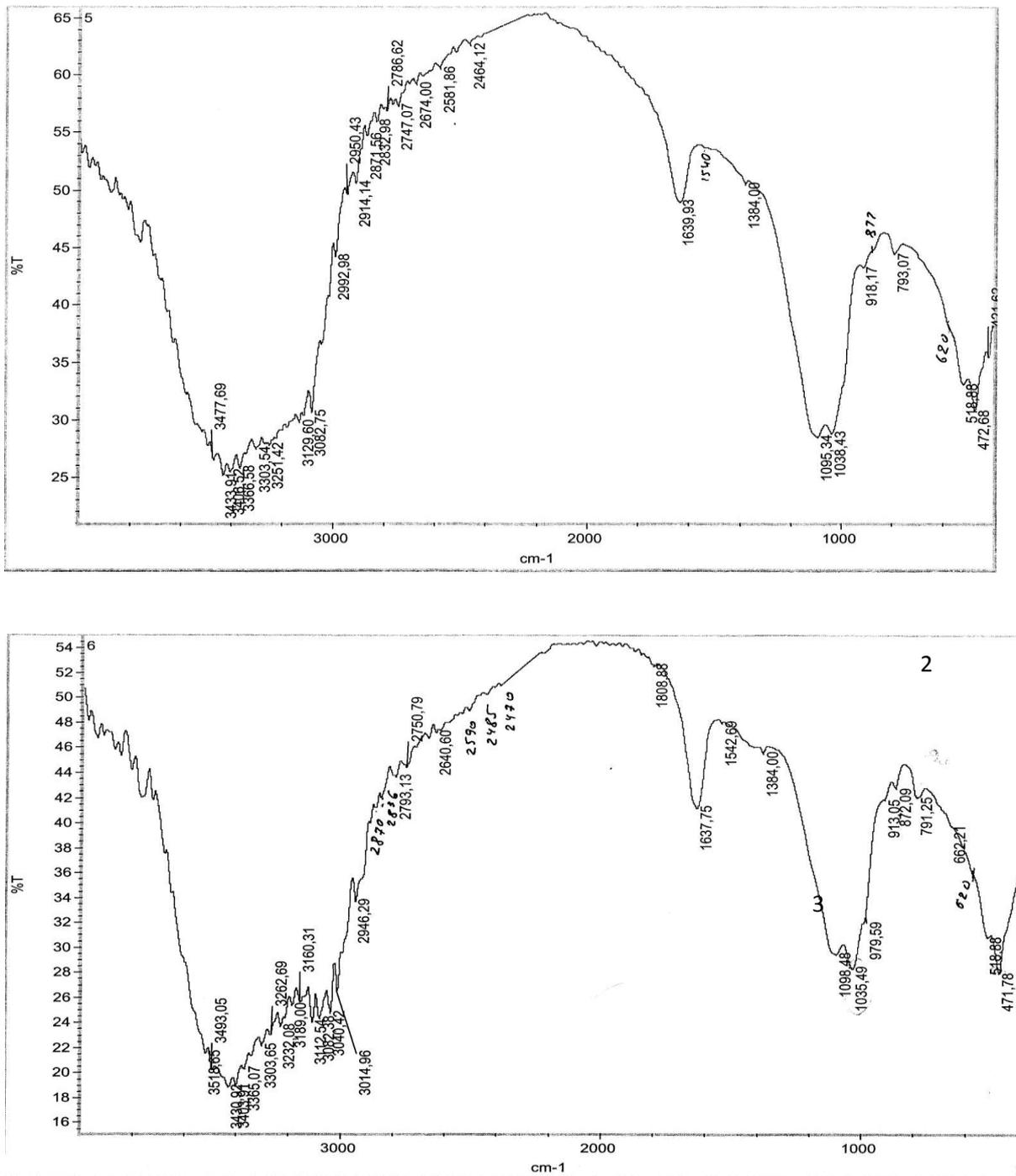
Methods and materials: In this paper, the composition, structure and properties of hydrotreating catalyst carriers have been studied using modern physicochemical methods of analysis such as infrared spectroscopy, X-ray phase and X-ray structure analysis as well as differential thermogravimetric analysis. And for hydrotreatment of diesel fuel they chose nickel-molybdenum with  $\text{NiO}:\text{MoO}_3$  mole ratio = 1:1 in quantity from 10 to 30 % wt. and carbonate-Palygorskite clay and a mixture of carbonate-Palygorskite clay with aluminum hydroxide containing 25, 50, 75 % wt. as active components. Initial palygorskite clay is used as activated mineral acids ( $\text{H}_3\text{PO}_4$  and  $\text{HNO}_3$ ) and without activation. The prepared product was used as a carrier of active catalyst phase. Samples activated with 5%  $\text{H}_3\text{PO}_4$  and  $\text{HNO}_3$  acids were also prepared.

The results and their discussion.

X-rays of DRON-2,0 with Cu anticathode were taken to determine the individuality of the product obtained by synthesis. For calculation of interplane distances tables were used, and the relative intensity of the J/J line was determined as a percentage of the most expressed reflex in the maximum.

IR - spectra (Fig. 2) were recorded in the region of  $400\text{-}4000\text{ cm}^{-1}$  on the AVATAR - 360 spectrophotometer by Nicolet. To remove spectra, the technique of pressing a sample with potassium bromide was used.





**Fig. 2. IR spectra of initial and activated carbonate palygorskite. 1-original palygorskite carbonate; 2- carriers based on 10% activated H<sub>3</sub>PO<sub>4</sub> carbonate palygorskite; 3 carriers based on 5% activated H<sub>3</sub>PO<sub>4</sub> carbonate palygorskite.**

The analysis of interplane distances of samples 1-3 shows that they are not purely crystalline substances, but closer to amorphous compounds. Comparison of the found interplane distances shows that samples number 2 and number 3 do not differ significantly from each other.

IR - absorption spectrum of sample No. 2 (Fig. 2) is characterized by frequencies at 3478, 3434, 3407, 3367, 3304, 3251, 3130, 3083, 2983, 2950, 2914, 2873, 2833, 2787, 2747, 3674, 2582, 2464, 1640, 1540, 1384, 1095, 1038, 918, 877, 793, 519, 473, and 422 cm<sup>-1</sup>. Sample #3 (fig. 2. ) in IR - absorption spectrum has the following frequencies: 3519, 3493,

3431, 3404, 3365, 3304, 3263, 3232, 3189, 3160, 3113, 3082, 3040, 3015, 2946, 2870, 2836, 2751, 2641, 2590, 2485, 2470, 1809, 1638, 1543, 1384, 1098, 1035, 980, 913, 872, 791, 662, 519 and 472  $\text{cm}^{-1}$ .

The frequencies detected in the region 3519-3100  $\text{cm}^{-1}$  correspond to valence oscillations of O-H bond of water and phosphoric acid molecules. The bands found in the range of 1500-1200  $\text{cm}^{-1}$  correspond to the valence oscillations of P=O bond of phosphoric acid. The frequencies observed in the range 1638-1640  $\text{cm}^{-1}$  correspond to the deformation oscillation of the bond of OH water molecules and hydroxyl groups of phosphoric acid. The frequencies observed in the region 1100 - 850  $\text{cm}^{-1}$  correspond to the valence oscillations of phosphoric acid O-P-O bond. The bands detected in the region of 650-400  $\text{cm}^{-1}$  correspond to deformation oscillations of phosphoric acid O-R-O bond. The frequencies found at 1050-3, 800-1, 625-4 and 500-2  $\text{cm}^{-1}$  correspond to the valence oscillations of silicon oxide form  $[\text{SiO}_4]^{4-}$  [7].

Thus, analyses of IR spectra of prepared samples Fig. 2. (samples 1-3) show that the initial and treated with 5% and 10% orthophosphoric acid is not quite identical in its spectra. After processing, i.e., activation with 5 and 10% orthophosphoric acid in the spectra, the acid concentration has almost no effect on the sample structure. On this basis, the treatment of carbonate - palygorskite clay to prepare carriers for the synthesis of catalysts with 5% solution of orthophosphoric acid is sufficient.

The study on activity of developed catalysts and catalyst carriers was carried out at hydrotreatment of straight-run diesel distillate of Bukhara Refinery obtained from mixture of oil and gas condensate. Hydrotreatment was carried out at temperatures of 320-370 °C and hydrogen pressure of 3.5-4.5 MPa (Table 1).

Table 1.

**Results of hydro desulphurization of Bukhara Refinery diesel distillate at new catalysts at autoclave unit Catalyst ratio: feedstock=1:10**

№	Indicators	Exodus. raw material	C A T A L I Z A T O R S		
			HR-306	AHМП-1	AHМП-11M
1.	Unit operating mode: pressure, MPa; temperature, °C		3,5-4,5 320	3,5-4,5 320	3,5-4,5 320
2.	Raw material and hydrogenated product quality: hydrogenate yield,% vol. density, kg / m <sup>3</sup> coeff. refractions sulfur content,% wt. hydrogenation depth: sulfur compounds,%	833 1,4625 1,34	821 1,4105 0,145 89,1	831 1,4452 0,196 85,3	828 1,4120 0,144 89,3

3	Fractional composition, % , °C:				
	I.C.	202	80	170	146
	5	215	95	210	212
	10	223	108	228	227
	20	230	220	245	245
	30	249	229	254	255
	40	252	238	266	266
	50	255	251	275	276
	60	269	263	293	289
	70	285	283	310	307
	80	310	303	330	325
	90	328	329	347	345
	Output/ К.к.	93/360	97/360	94/360	96/360

From the data of Table 1 we can see that the depth of hydro desulphurization of raw materials on HR-306 catalyst is 89.1 %, on nickel-molybdenum catalyst it is 85.3 %, obtained on the carrier containing 50 % carbonate-Palygorskite clay (ANMP-1).

Under the same conditions on nickel-molybdenum catalyst produced on a modified carrier (ANMP-11M), the content of carbonate-Paligorskite clay is 89.3%, i.e. a modification of carbonate-Paligorskite clay with H<sub>3</sub>PO<sub>4</sub> and HNO<sub>3</sub> acid solutions leads to an increase in catalyst activity by about 30%.

The obtained results show that the obtained diesel fuel under the above conditions fully meets the requirements of O'zDSt 989:2001. Decrease of hydrogenation density, refractive index, sulfur content and others testify to the fact that hydrogenation, hydro desulphurization, etc. processes take place at the catalyst in one stage.

## 2. Conclusions

The possibility of using local raw material resources, in particular, carbonate-Palygorskite clay of Navbakhorskoye deposit for synthesis of carriers of catalysts for hydrotreatment of diesel distillate has been substantiated.

It was found that modification of carbonate-Palygorskite clay with phosphoric and nitric acids leads to 30% increase of catalyst catalytic activity during hydrotreatment of diesel distillate.

Thus, as a result of synthesis and testing of a number of catalyst samples, a catalyst sample was found for hydrotreatment of diesel distillate obtained with the use of modified carbonate-Palygorskite clay, which is not inferior in activity to an imported catalyst.

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